

REMARKS/ARGUMENTS

The amendment to Claim 13 is supported at page 7, lines 4-17, the paragraph bridging pages 13 and 14, and by the results in Figure 2 and Table 2. See pages 12-13. New Claims 27 and 28 are supported by page 7, line 23 – page 8, line 25. No new matter has been entered.

The Examiner has rejected Claims 13, 15-20, 24-25 and 27 under 35 U.S.C. 103(a) over Nezu (US 5,817,718), in view of Kono (US 6,235,432), optionally with Goldberg (US 5,804,263) or Hubbard (US 6,368,677), and further considering Iwasaki (US 5,213,722) or Hostettler (5,919,570) or Rogers (US 5,187,028). Furthermore, the Examiner has cited Paul (US 4,804,427), Shamouilian (US 5,753,132) and Onishi (US 5,202,025) in support of her rejections. Applicants respectfully traverse the rejection of Claims 13, 15-20, 24-25 and 27.

The present invention relates to a method of producing a grafted polymer electrolyte membrane comprising (i) providing a precursor membrane comprising a polymer which is capable of being graft copolymerized, (ii) exposing the surface of the precursor membrane to a plasma in an oxidative atmosphere comprising argon and oxygen to generate surface carbonyl groups and/or surface hydroxyl groups, (iii) graft-polymerizing a side chain polymer to the plasma treated precursor membrane, and (iv) introducing a proton conductive functional group to said chain polymer. As noted by the amendment to Claim 13, the surface groups generated by the plasma treatment remain at least in part on the membrane, thus providing greater adherence/adhesion and, as a result, better performance. In this regard the present invention marks a number of significant improvements over the prior art. The remarkably simple, but ingenious, method of separately plasma treating the surface before any grafting reaction is beneficial in two major respects: (i) the hydrophobic membrane can be converted to a hydrophilic surface by the treatment and (ii) it circumvents the problems of oxidizing and degrading the proton-conducting functional groups. Moreover, the enhanced adhesion reduces contact resistance and the high number of proton conductive functional

groups allows for high electrical conductivity. This ingenious invention further facilitates transport of water molecules into and away from the membrane allowing significant improvements in fuel cell performance.

Applicants note that the functionalized side-groups can be inherently hydrophilic, but typically the main-chain precursor membrane is hydrophobic (see, e.g., page 13, lines 28-33 of the originally filed specification). Therefore, an improvement in adhesion property is shown because “the surface of the hydrophobic portion becomes more hydrophilic” (i.e. because of the generation of hydrophilic carbonyl or hydroxyl groups) (see page 13, line 33 – page 14, line 2). In other words, to realize the benefits of improved fuel cell performance obtained by the Applicants, the plasma generated hydroxyl and carbonyl groups remain, at least in part, unaffected on the surface during subsequent grafting polymerization and attachment of proton conductive functional groups.

However, in reviewing the Office Action, Applicants note that the Examiner seems to think that the plasma treatment is used to prepare the polymeric films for subsequent graft polymerization (see page 4, lines 3-4 in the Office Action). It appears that this misunderstanding is at the root of the numerous rejections issued by the Examiner, as is the double patenting rejection.

In order to clarify the situation, Claim 13 has been amended, and in the section below the relevant points within each of the cited references will be discussed. Broadly, the Examiner has cited references wherein plasma treatment can be utilized to either (i) prepare radicals or reactive sites to facilitate grafting or (ii) to convert a hydrophobic surface to a hydrophilic surface. No reference suggests earlier plasma treatment followed by a separate, stand alone grafting step using a separate grafting initiator/method.

Both Nezu references (US 5,817,718 and US 6,242,123 B1) disclose that gamma irradiation produce radicals which allow grafting of styrene groups. The styrene groups are

then further functionalized with proton conductive side-groups which renders the surface hydrophilic. Kono also describe the formation of radicals, although by a plasma treatment, on polyolefin fibers in the graft polymerization of desired side-groups (see col. 7, lines 7-15). Onishi also describe the formation of radicals by a plasma treatment on hydrophobic porous membranes (see col. 11, lines 4-25 and col. 13, lines 26-39). Furthermore, Hostettler describes oxygen/argon plasma treatment followed by a nitrogen plasma treatment of a hydrophobic surface to produce free radicals in the graft polymerization of hydrophilic side-groups (see col. 19, lines 4-15). These references demonstrate that plasma treatment can be utilized to produce radicals on a surface in order to effect graft polymerization.

Shamouilian describes an argon or oxygen plasma that can produce reactive C=O and C-O functional groups on the surface of polypropylene and poly(ethylene terephthalate) to react and bond to ceramic and metal bases (see col. 10, lines 28-37). Goldberg describes a plasma surface treatment of a hydrophobic surface which generates activated species which are then reacted with oxygen to form peroxy and/or hydroperoxy groups. Note that in these references the reactive or activated sites are effectively “consumed” during the subsequent polymerization. Therefore, these references disclose producing reactive functional groups through a plasma treatment that do not remain and which participate in a distinct chemical modification.

Iwasaki describes the use of plasma on polypropylene resin fibers to produce a hydrophilic surface having hydroxyl and carboxyl groups (see col. 5, lines 8-17) as does Paul (see col. 4, lines 7-11). Rogers describes the use of a low pressure plasma treatment which introduces carbonyl groups as to produce a more wettable surface (see col. 3, lines 55-68). Hubbard similarly describes a corona treatment of a polymer to improve the wettability of a hydrophilic primer to the polymer (see col. 5, lines 51-55). These references illustrate only that plasma treatment can be utilized to simply produce hydrophilic surfaces.

Clearly, the prior art illustrates that plasma treatment can be utilized in various ways to achieve very different results. It appears that various treatments and operating conditions can lead to dramatically different results such as producing radicals, reactive sites, or simply a hydrophilic surface.

In the present invention, Applicants utilize a plasma treatment to convert the hydrophobic membrane to one possessing a hydrophilic surface containing hydroxyl and/or carbonyl groups. The plasma treatment is then followed by a separate grafting reaction utilizing, for example, electron beam irradiation, and a subsequent functionalization step.

Applicants note that the Examiner has stated, in various correspondences, her belief that the peroxy and hydroperoxy groups in Goldberg can be viewed as similar analogues of the plasma treatment-produced hydroxyl and carbonyl groups of the invention. If this were true, however, Goldberg would effectively teach away from the invention wherein plasma-generated hydrophilic groups remain on the surface, because in Goldberg the plasma-generated groups all subsequently react. Similar arguments can be made of the plasma treatments which cause reactive functional groups or radicals on the polymer surfaces as in Shamouilian, Kono, Onishi, and Hostettler. Applicants note that the plasma treatment in these references produces a different type of a surface than the finished surfaces required by the present invention. Therefore, these references cannot suggest the present invention.

As noted in the specification, plasma treatment *prior* to grafting and functionalization is a significant improvement over each of the cited references. For example, the simple grafting and functionalization of the grafted chains, without the plasma treatment, to increase hydrophilicity would still lead to hydrophobic main chains which lead to poorer fuel cell performance (see the Examples and Table 2 in page 13). Alternatively, plasma treatment of a membrane which already contains proton conductive grafted side-chains, in the hopes of

improving hydrophilicity/adhesion, will also inevitably lead to degradation in the overall performance of the fuel cell as the functional groups are oxidized (see page 5, lines 5-11).

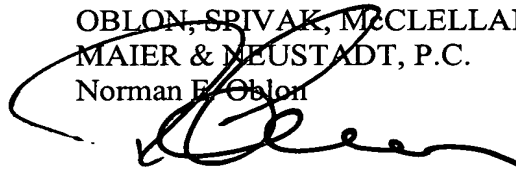
In another words, not only is the combination of the various steps important, but the order in which they are carried out is critical. Withdrawal of the rejection is respectfully requested.

The detailed discussion, in the previous section, discussing the fundamental differences between the prior art and the invention obviates the double patenting rejection, as well.

Applicants respectfully submit that the application is now in condition for allowance. Early notification of such allowance is earnestly solicited.

Respectfully submitted,

OBLON, SPIVAK, MCCLELLAND,
MAIER & NEUSTADT, P.C.
Norman F. Oblon



Richard L. Treanor
Registration No. 36,379

Customer Number
22850

Tel: (703) 413-3000
Fax: (703) 413 -2220
(OSMMN 08/03)